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STRUCTURE OF A LAMELLAR PHASE FORMED BY NON-IONIC SURFACTANT AND WATER
Effects of shear flow

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Abstract

We have investigated effects of shear flow on the structure of lamellar phase in hepta(oxyethylene glycol)–*n*–hexadecylether–water system using small-angle neutron scattering (SANS) under shear flow at the shear rates ($\dot{\gamma}$) from 10^{-3} s^{-1} to 50 s^{-1}. In the range $\dot{\gamma}$=10^{-2} ~1 s^{-1}, significant changes have been observed in both intensity and position of the reflection peak. Small-angle X-ray scattering without shear has been also measured at various concentrations and temperatures. It has been suggested from these results that the shear flow causes contraction of lamellar domains and formation of a new domain composed of disrupted bilayers which grows rapidly with increasing shear rate and reconstructs original microstructures.

Keywords: bilayers, lamellar phase, SANS, SAXS, shear, small-angle scattering, surfactant

Introduction

Surfactant–water systems form a lamellar phase composed of bilayers when appropriate conditions (surfactant concentration, temperature, and concentration of additives such as salt and cosurfactant) are satisfied. In recent years, effects of shear flow on the structure of a lamellar phase have been studied by using small-angle neutron scattering (SANS), small angle light scattering (SALS), and ^{2}HNMR. Diat *et al.* [1] have measured SANS and SALS on a quaternary mixture of sodium dodecyl sulfate, pentanol, water, and dodecane. They have found that the lamellar phase is changed into multilayered vesicles above a certain shear rate depending on the composition. Similar conclusion has been obtained on non-ionic surfactant ($C_{12}E_4$ and $C_{12}E_6$)–water systems by using ^{2}HNMR [2] (C_nE_m is an abbreviation of $C_nH_{2n+1}(OC_2H_4)_mOH$). Weigel *et al.* [3] have reported that elongated vesicles are formed at higher shear rates based on the measurements of SANS and SALS on the $C_{12}E_4$–water system.

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These measurements have been performed in a range of shear rate $\dot{\gamma}=1\sim5\cdot10^3$ s^{-1}. In the present contribution, we have measured SANS paying attention to the behaviors at the low shear rates, i.e., $\dot{\gamma}=10^{-3}\sim10^2$ s^{-1} on a non-ionic surfactant ($C_{16}E_7$)–water system. This system was chosen because phase behaviors have been studied previously by us [4, 5]. However, we have made more detailed phase diagram in this study by using ^{2}H NMR. Before performing SANS measurements under shear flow, small-angle X-ray scattering (SAXS) has been measured without shear to investigate variation in static structures with temperature and concentration.

Experimental

$C_{16}E_7$ was purchased from Nikko Chemicals, Inc. in crystalline form (>98%) and used without further purification. Deuterium oxide purchased from ISOTEC, Inc. (99.9%) was used after being degassed by bubbling of nitrogen to avoid oxidation of the ethylene oxide group of surfactants.

Small-angle X-ray scattering was measured using an apparatus (MAC Science) constructed from X-ray generator (SRA MXP18, 18kW), incident monochromater (W/Si multilayer crystal), Kratky slit, and imaging plate (DIP 200). Details of the apparatus have been reported already [6].

Measurements of SANS were carried out at the instrument SANS-U of Institute for Solid State Physics of University of Tokyo in Tokai with a Couette shear cell. The sample-to-detector distance was chosen to be 1.5 m for all runs. The momentum transfer was $0.3<q<1.4$ nm^{-1} ($q=(4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and $\lambda=0.7$ nm is the neutron wavelength). The wave length resolution, $\Delta\lambda/\lambda$, is 0.1. All the measurements were made for the sample containing 55 wt% of $C_{16}E_7$ at 328 and 343 K.

Results and discussion

Phase diagram

Figure 1 shows a phase diagram of the $C_{16}E_7$–D_2O system. Although essential features are almost the same as that reported before, two-phase coexistence has been

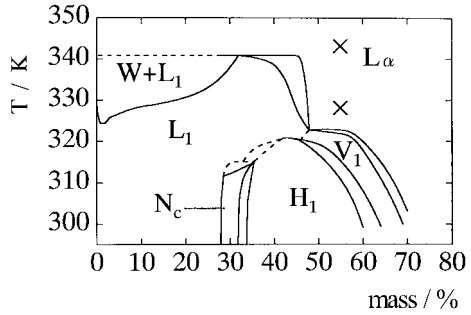

Fig. 1 Phase diagram of the $C_{16}E_7$–D_2O system. L_1, micellar phase; W+L_1, coexistence of two liquid phases, N_c, nematic phase; H_1, hexagonal phase; V_1, bicontinuous cubic phase; L_α, lamellar phase. The crosses indicate SANS measurements under shear flow

found between micellar and lamellar phases, lamellar and cubic phases, cubic and hexagonal phases, and nematic and hexagonal phases. We found two-phase coexistence also between micellar and nematic phases as well as micellar and hexagonal phases. However, the phase boundary could not be determined definitely and so indicated by the dashed lines in Fig. 1.

Small-angle X-ray scattering without shear

In Fig. 2, the lamellar spacing d obtained from the first-order-reflection of SAXS is plotted against the volume fraction of the hydrocarbon chain (Φ_{hc}) calculated from the volume of each functional group found in literature [7, 8]. When the thickness of the hydrocarbon layer (d_{hc}) is constant, the following relation holds between d and Φ_{hc}.

$$d=d_{hc}/\Phi_{hc} \quad (1)$$

Equation (1) indicates that the double logarithmic plot in Fig. 2 should be straight line with a slope –1. The observed slope at 348 K is exactly the same as this prediction. The thickness d_{hc} is obtained to be 1.88 nm from this plot. Below 338 K, however, the plot deviates from the straight line and the absolute value of the slope decreases as the temperature decreases. At 328 K, the slope becomes close to –1/2 which is expected for the ordered structure composed of one-dimensional aggregates with a constant cross-section such as a hexagonal phase. However, we could not observe any characteristic peak other than the first- and second-order reflections from lamellae.

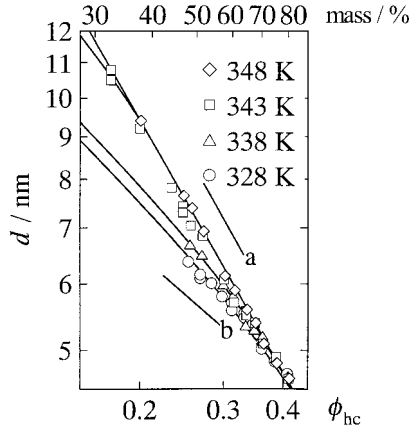

Fig. 2 Double logarithmic plots of the lamellar spacing d obtained from the first-order-reflection of SAXS *vs.* volume fraction of the hydrocarbon chain (Φ_{hc}). The solid lines a and b indicate the slope –1 and –1/2, respectively

These results suggest that the bilayer has water-filled defects in the lower temperature range. The existence of such defects has been already reported for the $C_{16}E_6$–D_2O system [5–7] and referred to a 'random mesh' (L_α^H) phase although de-

tailed structures are still unclear. If d_{hc} is independent of temperature, the observed decrease of d with decreasing temperature corresponds to the increase in the fraction of the defects.

Small-angle neutron scattering under shear flow

Figure 3 shows contour plots of SANS intensity under shear flow using the neutron beam passed through the center of the Couette cell (parallel to both the flow direction and the velocity gradient) at 343 K. The direction of the abscissa is parallel to the shear flow while the direction of the ordinate (referred to 'neutral' direction) is perpendicular to both shear flow and velocity gradient.

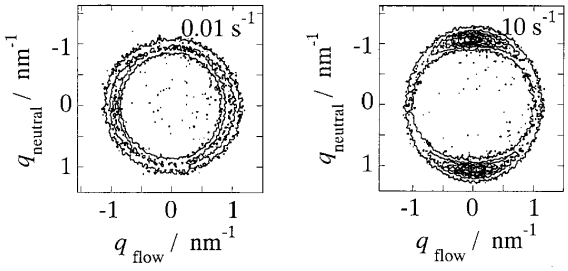

Fig. 3 Contour plots of SANS intensity under shear flow using the neutron beam passed through the center of the Couette cell (parallel to both the flow direction and the velocity gradient) at 343 K. The direction of the abscissa is parallel to the shear flow while the direction of the ordinate (referred to 'neutral' direction) is perpendicular to both shear flow and velocity gradient

Scattering intensities for the flow and neutral directions integrated over a sector of ±10 at 343 K at different shear rates are shown in Figs 4a and 4b, respectively. The observed scattering peaks in Figs 4a and 4b correspond to the diffraction from the domains where lamellae are ordered perpendicular to the flow and neutral directions, respectively.

In the range $\dot{\gamma}=10^{-3}$–10^{-1} s^{-1}, the peak intensities for both directions decrease with increasing shear rate without change in the peak position, q_{max}. We have made preliminary measurements using a neutron beam passed through the side of the Couette cell (neutron beam parallel to the flow direction) and again found the decrease in the peak intensity. These results indicate that the decrease in the peak intensity is not due to the ordering of the lamellae along a certain direction but due to the decrease in the domain size itself.

At the shear rate of $\dot{\gamma}=3\cdot10^{-2}$ s^{-1}, a new peak appears at higher q values. As the shear rate increases further, this new peak is shifted to the lower q values and approaches the q_{max} of the original peak. On the other hand, the original peak itself disappears at higher shear rates. The intensity of the new peak for the neutral direction rapidly increases with increasing shear rate, which corresponds to ordering of lamellae parallel to both the flow direction and the velocity gradient.

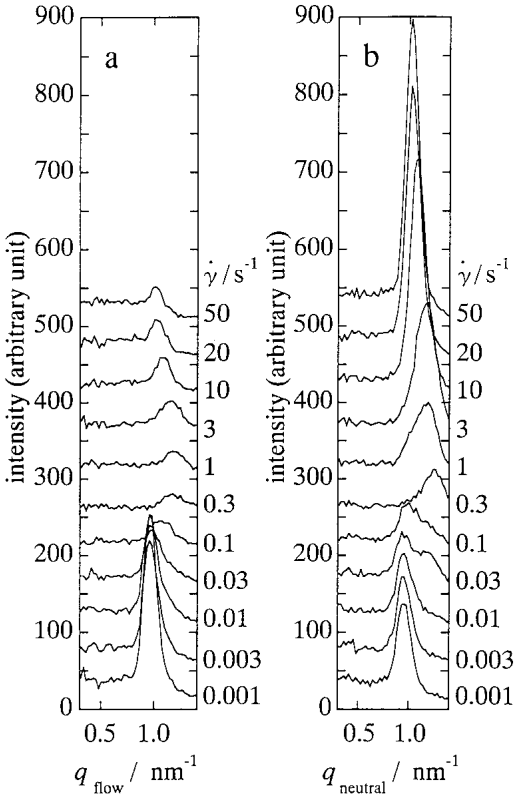

Fig. 4 Scattering intensities for the flow (a) and neutral (b) directions integrated over a sector of $\pm 10^{o}$ at different shear rates at 343 K

Similar results have been obtained at 328 K. Although the q_{max} of the original peak is higher than at 343 K, the q_{max} of the new peak is almost the same as that at 343 K. This suggests that the appearance of the new peak corresponds to the formation of a new domain whose microstructure is independent of temperature.

Taking into account the SAXS results without shear, we can infer the following scenario for the effects of shear on the structure of the lamellar phase. As the shear rate increases from $\dot{\gamma}=10^{-3}$ up to 10^{-1} s^{-1}, the lamellar domains contracts into smaller domains. At the shear rates of $3 \cdot 10^{-2}$ s^{-1}, a new domain is formed composed of disrupted bilayers ordered parallel to both the flow direction and the velocity gradient. As the shear rate increases further, such domains grow rapidly accompanying the reduction of defects until the original microstructure is reconstructed.

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